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Formation mechanism of titanium silicide by mechanical alloying

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The syntheses of five titanium silicides (Ti_3Si, $TiSi_2$, Ti_5Si_4, Ti_5Si_3, and TiSi) by mechanical alloying (MA) have been investigated. Rapid, self-propagating high temperature synthesis (SHS) reactions were involved in producing the last three materials during room temperature high-energy ball-milling of elemental powders. Such reactions appeared to occur through ignition by mechanical impact in the fine powder mixture formed after a critical milling period. From *in-situ* thermal analyses, each critical milling period for the formation of Ti_5Si_4, Ti_5Si_3, and TiSi was observed to be 22, 35.5 and 53.5 minutes, respectively. However, the formation of Ti_3Si and $TiSi_2$ did not occur even after 360 minutes of milling of as-received Ti and Si powder mixture, due to the lack of homogeneity of the powder mixture. Other ball-milling procedures were employed for the syntheses of Ti_3Si and $TiSi_2$ using different sizes of Si powder and milling medium materials. Ti_3Si was synthesized by milling a Ti and 60 minutes premilled Si powder mixture for 240 minutes. α-$TiSi_2$ and $TiSi_2$ were produced by high energy partially stabilized zirconia (PSZ) ball-milling for 360 minutes in a steel vial followed by jar-milling of a Ti and 60 min premilled Si powder mixture for 48 hr. The formation of Ti_3Si and $TiSi_2$ occurs through a slow solid state diffusion reaction, and the product(s) and reactants coexist for a certain period of time. The formation of titanium silicides by MA and the reaction rate appeared to depend on the homogeneity of the powder mixture, milling medium materials, and heat of formation of the product involved. © *2001 Kluwer Academic Publishers*

1. Introduction

The synthesis of nanocrystalline intermetallics with high melting points [1, 2] via mechanical alloying (MA) has been attempted in numerous studies. Materials include Ni- and Cu-aluminides [3–7], carbides such as TiC [8], and Mo-silicides [9–13]. In general, combustion reactions have been initiated by ball-milling in a variety of highly exothermic reaction mixtures. The formation of intermetallics from their elemental components accelerates during ball-milling to become a self-sustaining high temperature reaction [14, 15]. The major advantages of this processing method are higher energy efficiency, higher productivity, shorter processing cycle times, and better purification capability than the conventional reaction process [16].

Titanium silicides have attracted more interest recently because a number of their properties have potential in materials applications. Characteristics which make them promising high temperature structural materials include low temperature toughness, high temperature strength and creep resistance, oxidation resistance, and relatively low density [17, 18]. They can also be used in microelectronics as interconnections and diffusion barriers for integrated circuits, where low electrical resistivity and chemical compatibility with silicone substrates have resulted in a variety of applications [17]. Their high thermal and electrical conductivity also make them attractive materials for the design of new optical carriers of information that require high stability and resistance [19].

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In spite of their research significance, in recent years there have been relatively few studies on the preparation of titanium silicides by means of MA [2, 20–22]. This can be attributed to poor conversion of reactants to the desired titanium silicide. Optimizing the processing variables is expected to be a key issue for the products. For better control of the process, an understanding of the formation mechanism(s) of titanium silicides [23] by MA is essential. In this paper, experimental studies have been designed to achieve a better conversion of reactants to the product via MA. The main focus has been on elucidating the formation mechanism of the product. Mechanical alloying of titanium silicides such as Ti_5Si_4, Ti_5Si_3, TiSi, Ti_3Si, and $TiSi_2$ has been emphasized in this paper.

2. Experimental

Mechanical alloying (MA) was performed using Spex 8000D Mixer/Mills (SPEX Industries, Inc.) and cylindrical partially stabilized zirconia (PSZ) or steel vials (38 mm in inner diameter and 52 mm long). Element powders and high Cr hardened steel or PSZ balls (12.7 mm and 6.4 mm diameters) were placed in the vial in an Ar-flushed glove box to avoid excessive oxidation. The mass of the powder charge was 7 g. The mass ratio of ball to powder was 5 : 1 in all cases. The average powder particle sizes of as-received Ti and Si were 72.1 μm and 19.1 μm, respectively. The purity of the powders was better than 99.95%. For each designed phase, the charged atomic ratio of the reactants corresponded to the reaction stoichiometry. When transformation to titanium silicide failed with this procedure, another ball-milling procedure of the element powders was employed that utilized different sizes of Si powder and milling medium materials.

The phase composition of the reaction products was investigated by X-ray diffraction (XRD) using Cu K_α radiation. In order to monitor the progress of the reaction, each heating curve measurement was obtained by *in-situ* thermal analysis using a type K non-contact infrared thermometer (sensitivity: ±2 °C).

3. Results and Discussion

3.1. Syntheses of Ti_5Si_4, Ti_5Si_3, and TiSi

3.1.1. Synthesis of Ti_5Si_4

XRD patterns of the steel ball-milled Ti-44.4 at. % Si powder mixture in a PSZ vial at various MA times are shown in Fig. 1. The XRD patterns after 20 minutes of milling show that no reaction at all had occurred, as indicated by the presence of the sharp peaks of the starting elements Ti and Si. Increasing the milling time up to 23 minutes caused total disappearance of Ti peaks and significant reduction of Si peaks as well as formation of some Ti_5Si_3, low temperature phase (LT) Ti_5Si_4, and high temperature phase (HT) Ti_5Si_4. After 60 minutes of MA, peaks corresponding to elemental Si completely disappeared and complete transformation to intermetallic compounds was obtained. It can be seen that the lower energetic input such as shorter milling time favors the formation of the low temperature phase of Ti_5Si_4, while the longer milling time promotes formation of the high temperature phase. This result is in good agreement with thermodynamics.

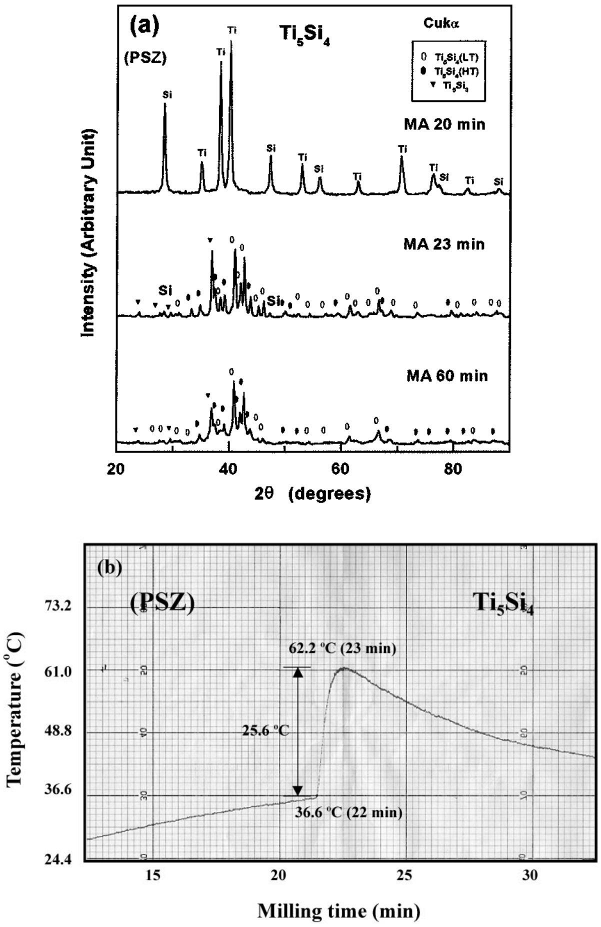

Figure 1 (a) XRD patterns of the steel ball-milled Ti-44.4 at. % Si powder mixture in a PSZ vial at various MA times, (b) *in-situ* thermal analysis of Ti-44.4 at. % Si powder mixture with respect to milling time.

To correlate the milling time with the thermal behavior of the reaction, *in-situ* thermal analysis of Ti-44 at. % Si powder mixture with respect to milling time was obtained as shown in Fig. 1b. The temperature of the middle of the vial wall slowly increased from 25.6 °C to 36.6 °C after 22 minutes of milling and reached 62.2 °C in about 1 minutes. Instant ignition is clearly indicated by the abrupt temperature increase. After 120 minutes of milling, the temperature decreased to 40.2 °C while the ambient temperature was 23 °C. Considering the sudden exothermic reaction process, the reaction of elemental Ti and Si to form Ti_5Si_4 under current condition can be attributed to a self-propagating high-temperature synthesis (SHS) reaction similar to that observed previously by Kachelmyer *et al.* [21].

3.1.2. Synthesis of Ti_5Si_3

Fig. 2a shows XRD patterns of the steel ball-milled Ti-37.5 at. % Si powder mixture in a PSZ vial at various MA times. Increasing milling time up to 30 minutes causes considerable reduction of both Ti and Si peak intensities and formation of trace amounts of Ti_5Si_3. Increasing the milling time to 36.5 minutes leads to almost complete disappearance of both Ti and Si peaks and formation of Ti_5Si_3 and trace amounts of LT Ti_5Si_4. After 60 minutes of milling, complete transformation

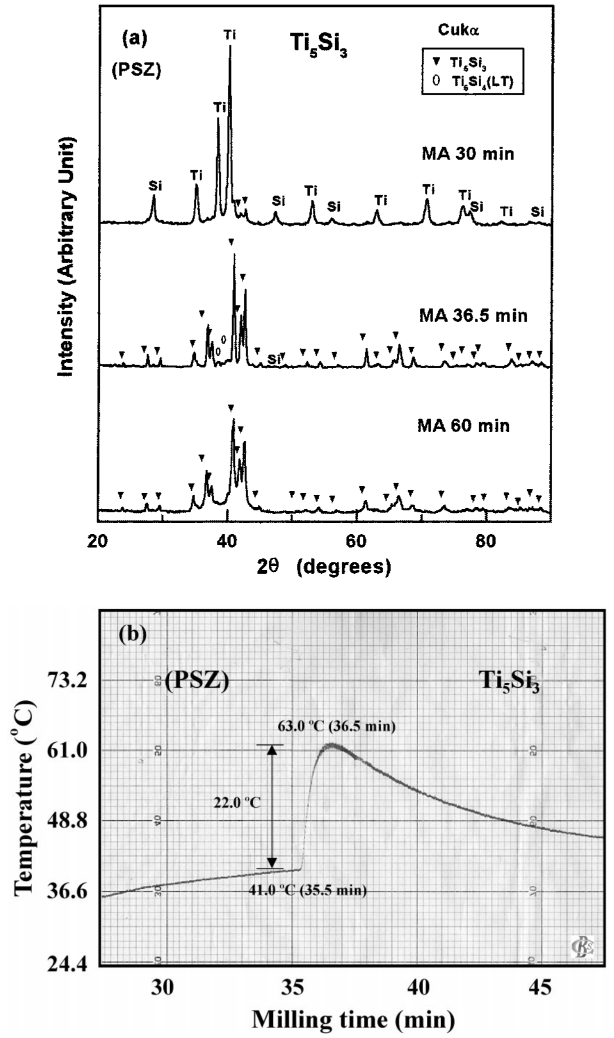

Figure 2 (a) XRD patterns of the steel ball-milled Ti-37.5 at. % Si powder mixture in a PSZ vial at various MA times, (b) *in-situ* thermal analysis of Ti-37.5 at. % Si powder mixture with respect to milling time.

to Ti_5Si_3 occurred. In general peak intensities corresponding to Ti_5Si_3 decreased with increased milling time, which can be attributed to further size reduction of the Ti_5Si_3 particles.

In-situ thermal analysis of Ti-37.5 at. % Si powder mixture with respect to milling time is shown in Fig. 2b. The temperature of the middle of the vial wall suddenly increased from 40.2 °C to 63 °C after 36.5 minutes of milling. It thus appears that the abrupt reaction process at 36.5 minutes is also governed by a SHS reaction.

3.1.3. Synthesis of TiSi

XRD patterns of the steel ball-milled Ti-50.0 at. % Si powder mixture in a PSZ vial at various MA times are shown in Fig. 3a. 30 minutes of milling produced no reaction at all. Increasing the milling time up to 54.5 minutes leads to complete disappearance of Ti peaks and coexistence of intermetallics such as LT and HT Ti_5Si_4, and TiSi as well as trace amounts of Si. After 90 minutes of milling, peaks of Si completely disappeared, which can be attributed to dissolution of Si in Ti_5Si_4.

In-situ thermal analysis of the Ti-50.0 at. % Si powder mixture with respect to milling time is shown in Fig. 3b. The temperature of the middle of vial wall suddenly increased from 40.2 °C to 62.8 °C in about 1 minute after 54.5 minutes of milling and then slowly decreased to 41.4 °C after 120 minutes of milling. The sudden exothermic reaction process at 54.5 minutes can also be attributed to a SHS reaction (of TiSi).

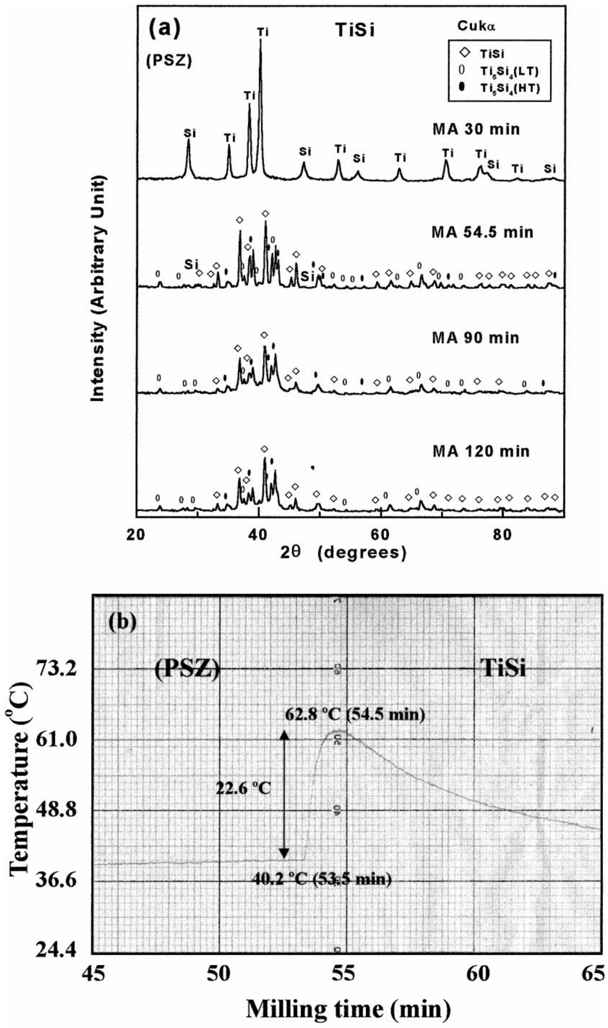

Figure 3 (a) XRD patterns of the steel ball-milled Ti-50.0 at. % Si powder mixture in a PSZ vial at various MA times, (b) *in-situ* thermal analysis of Ti-50.0 at. % Si powder mixture with respect to milling time.

The formation mechanism of Ti silicides such as Ti_5Si_4, Ti_5Si_3, and TiSi by MA under current experimental conditions can not be explained by a solid state interface diffusion reaction. The mechanical impact during ball milling can not produce high enough energy to alloy the powder mixture in such a short period of MA in the absence of a sudden exothermic reaction. It usually takes as much as 10–20 hours to alloy a powder mixture through a solid state interface diffusion reaction mechanism [24, 25]. It was reported that it is impossible to obtain a SHS reaction below 1500 K and difficult between 1500 K and 2000 K [26]. However, by applying ignition or MA, a SHS reaction is possible in these temperature ranges [26]. It was also reported that important conditions for the SHS reaction are: the heat of formation (ΔH_{298}) of the product must have a large negative value and/or the mean particle size of powder mixture must reach a critical value [27]. Since a powder mixture having higher deformation and higher density of defects reduces the required ignition temperature,

TABLE I Critical milling times for the SHS reactions of Ti_5Si_4, Ti_5Si_3, and TiSi, and heats of formation of titanium silicide

Compounds	ΔH (kJ/mol.at.)	Critical milling time (min)
Ti_5Si_4	−81.0	22.0
Ti_5Si_3	−72.5	35.5
TiSi	−64.9	53.5
Ti_3Si	−53.0	N/A
$TiSi_3$	−44.8	N/A

the SHS reaction can easily take place in a short period of milling.

Under current experimental conditions, the SHS reaction may occur in one particle or a small local volume of the powder mixture having a critical particle size, since the particle size distribution of the powder mixture is in general heterogeneous. Once triggered by the mechanical impact, the large heat of formation of Ti silicide (Ti_5Si_4, Ti_5Si_3, and TiSi) supplies the energy for igniting the neighboring region and the reaction becomes self-sustaining. This implies that the powder mixture after a certain period of ball-milling reaches a critical value of average particle size fine enough to accept an easy ignition by the mechanical impact. It can thus be concluded that the formation mechanism of Ti_5Si_4, Ti_5Si_3, and TiSi by MA under current condition is the SHS reaction. It is also confirmed that the critical milling times for the SHS reaction depend on the absolute value of the heat of formation of the product, as listed in Table I.

3.2. Syntheses of Ti_3Si and $TiSi_2$

3.2.1. Synthesis of Ti_3Si

XRD patterns of the steel ball-milled Ti-25.0 at. % Si powders in a PSZ vial at various MA times are shown in Fig. 4a. XRD patterns after 60 minutes of milling show coexistence of trace amounts of Ti_3Si and LT Ti_5Si_4, and elemental Ti and Si. Increased milling times up to 240 minutes, produce no significant changes in the XRD patterns. The persistence of elemental Ti and Si, and incomplete transformation to Ti_3Si by MA under current conditions were considered to be due to the heterogeneous nature of the Ti/Si powder mixture, i.e., the vol. % of Si in the powder mixture was much smaller than that of Ti and the mean particle size of the Si powder was relatively large compared to that of the Ti powder. It was also thought that the ductile Ti powder could easily adhere to the container vial wall before being homogeneously mixed with the brittle Si powder even in a short period of milling. Therefore in order to improve the uniform mixture of Ti and Si powders, as-received Si powder was mechanically ball-milled using the same spex mill before applying a high energy ball-milling procedure. As a result, the Si powder with a mean particle size of 3 μm was obtained.

Resulting XRD patterns of the Ti-25.0 at. % premilled Si powder mixture in a PSZ vial after ball-milling at various MA times are shown in Fig. 4b. Increasing the milling time up to 120 minutes causes formation of trace amounts of Ti_3Si and Ti_5Si_3. After 180 minutes of milling, elemental Ti and Si peaks completely disappeared, resulting in complete transformation to both Ti_3Si and Ti_5Si_4. Increasing the milling time up to 240 minutes leads to more favorable formation of crystalline titanium silicide. The milled samples were further examined by SEM. Resulting SEM micrographs of a cross sectional 240 minutes ball-milled Ti-25.0 at. % as-received Si powder mixture and a Ti-25.0 at. % 60 minutes premilled Si powder mixture are shown in Fig. 5a and b, respectively. Fig. 5a shows that no alloying process is observed when using the

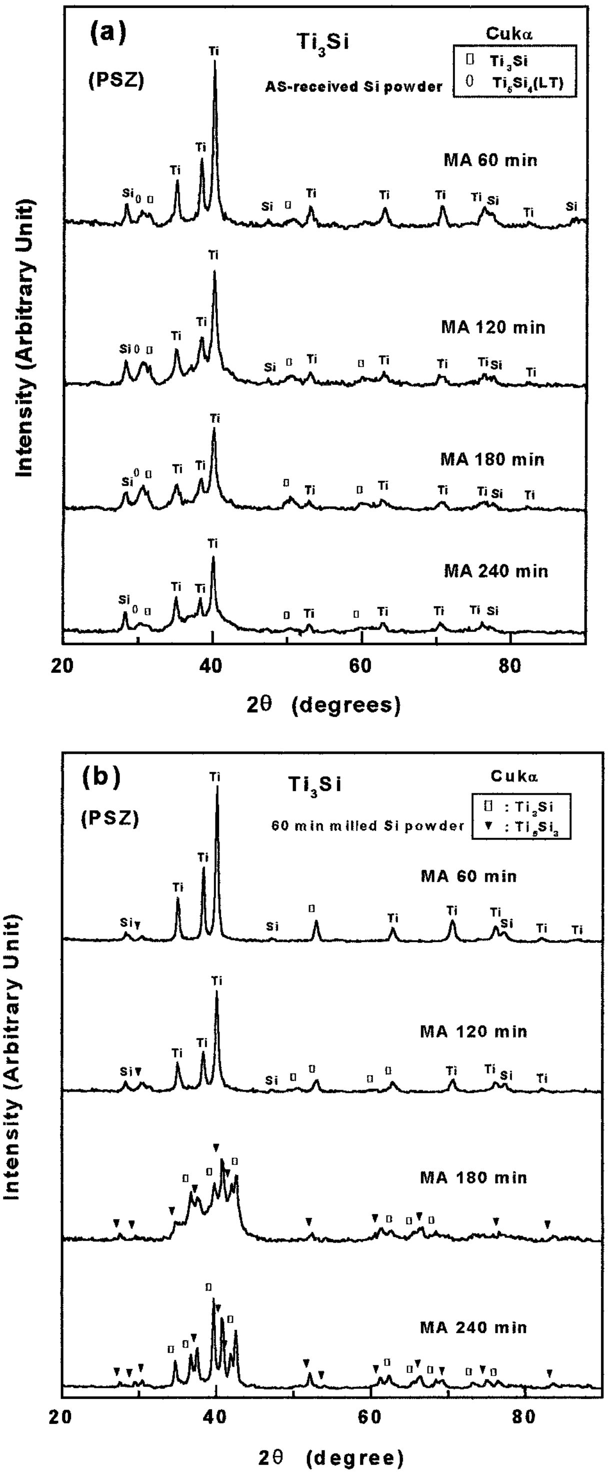

Figure 4 XRD patterns of the steel ball-milled Ti-25.0 at. % Si powder mixture in a PSZ vial at various MA times (a) as-received Si powder and (b) 60 min premilled Si powder.

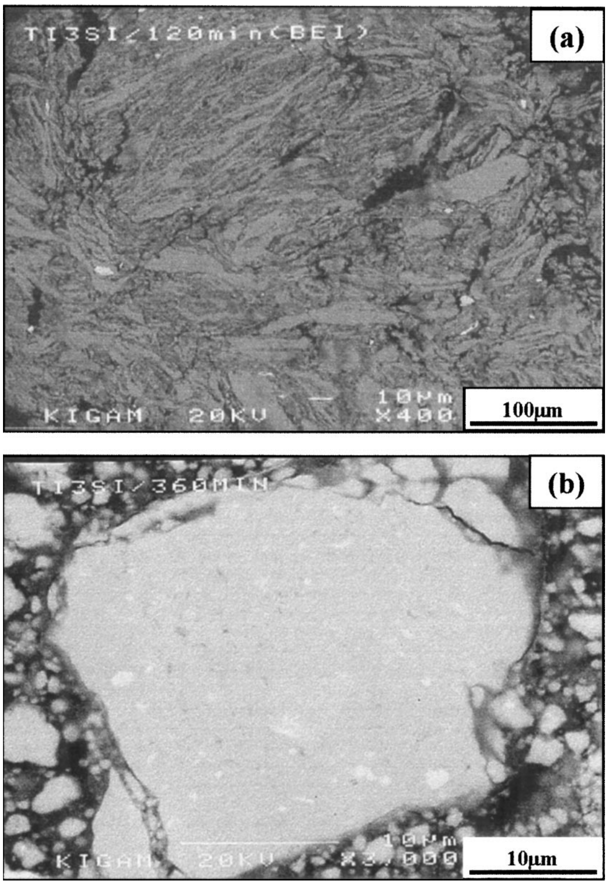

Figure 5 SEM micrographs of cross-sectional Ti-25.0 at. % Si powders mechanically alloyed for 240 min by means of a PSZ vial and steel balls (a) as-received Si powder and (b) 60 min premilled Si powder.

as-received Si powder. The Ti particles are in light contrast and the Si particles are in dark contrast. On the other hand, homogeneous structures are achieved when using the premilled Si powder, as shown in Fig. 5b. The SEM observations are thus in good agreement with the x-ray results.

3.2.2. Synthesis of $TiSi_2$

Fig. 6 shows XRD patterns of steel ball-milled Ti-66.7 at. % Si powders in a PSZ vial at various MA times. XRD patterns after 120 minutes of milling show coexistence of some α-$TiSi_2$ peaks as well as elemental Ti and Si peaks. Increasing milling time up to 180 minutes produces no significant changes in the XRD patterns. The lack of complete transformation to $TiSi_2$ even after 360 minutes of milling is again considered to be due to the heterogeneous nature of the Ti and Si powders, and adhesion of ductile Ti powder to the vial wall due to heat generation.

A steel vial, which has higher conductivity, was used with PSZ balls to increase the yield of $TiSi_2$. This procedure reduces adhesion of the ductile Ti powder to the vial walls by improved dissipation of the heat generated during high energy ball-milling. Resulting XRD patterns of the PSZ ball-milled Ti-66.7 at. % Si powder mixture in a steel vial at various MA times are shown in Fig. 7a. The XRD patterns after 120 minutes of milling show that no reaction at all had occurred, similar to the previous result. However, increased milling time up to 180 minutes causes considerable reduction of Ti and Si peaks as well as formation of some α-$TiSi_2$ and $TiSi_2$. Increasing the milling time up to 360 minutes leads to coexistence of α-$TiSi_2$, $TiSi_2$, and TiSi peaks as well as elemental Ti and Si peaks. Compared to the XRD result shown in Fig. 6, more peaks corresponding to α-$TiSi_2$ were observed between 180 and 360 minutes of milling. Under current conditions, it is therefore difficult to synthesize $TiSi_2$ by changing only the milling medium materials.

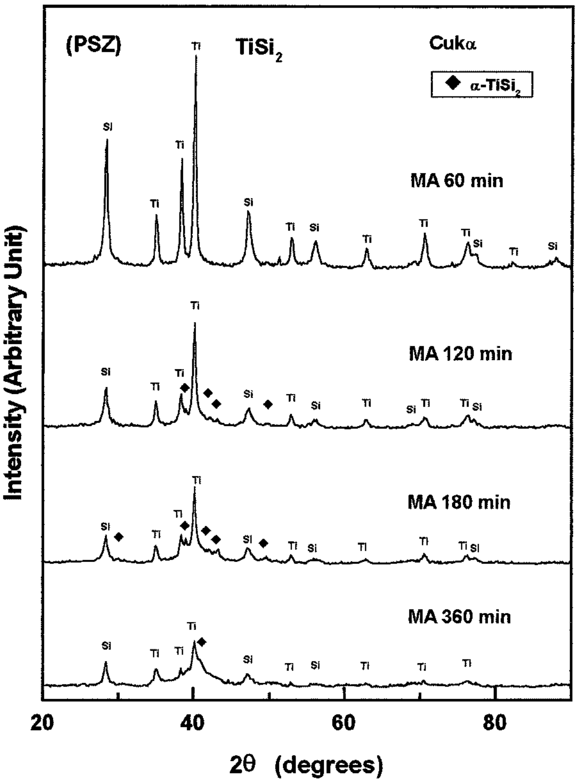

Figure 6 XRD patterns of the steel ball-milled Ti-66.7 at. % Si powder mixture in a PSZ vial at various MA times using as-received Si powder.

Another mechanical alloying procedure employed a steel vial, PSZ balls, and a 48 hr milled Ti-66.7 at. % 60 min premilled Si powder mixture. Resulting XRD patterns at various MA times are shown in Fig. 7b. After 120 minutes of milling, XRD peaks corresponding to α-$TiSi_2$ appeared. Increasing milling time up to 360 minutes causes total disappearance of both Ti and Si peaks and formation of significant amounts of α-$TiSi_2$ as well as trace amounts of $TiSi_2$. However, increasing milling time up to 720 minutes leads to no significant change in the XRD patterns. The milled samples were further examined by SEM. Resulting SEM micrographs of cross sectional Ti-66.7 at. % Si powders ball-milled for 360 minutes by means of a steel vial and PSZ balls using as-received Si powder, and 60 minutes premilled Si powder and a 48 hr jar-milled powder mixture are shown in Fig. 8a and b, respectively. As shown in Fig. 8a, phase structures showing coexistence of Ti (light) and Si (dark) can be observed. Fig. 8b indicates that the reactions of Ti and Si are almost complete producing a homogeneous $TiSi_2$ phase. The SEM observation is thus in good agreement with the x-ray results.

In situ thermal analyses corresponding to both Figs 4b and 7b are shown in Fig. 9. Even with increased

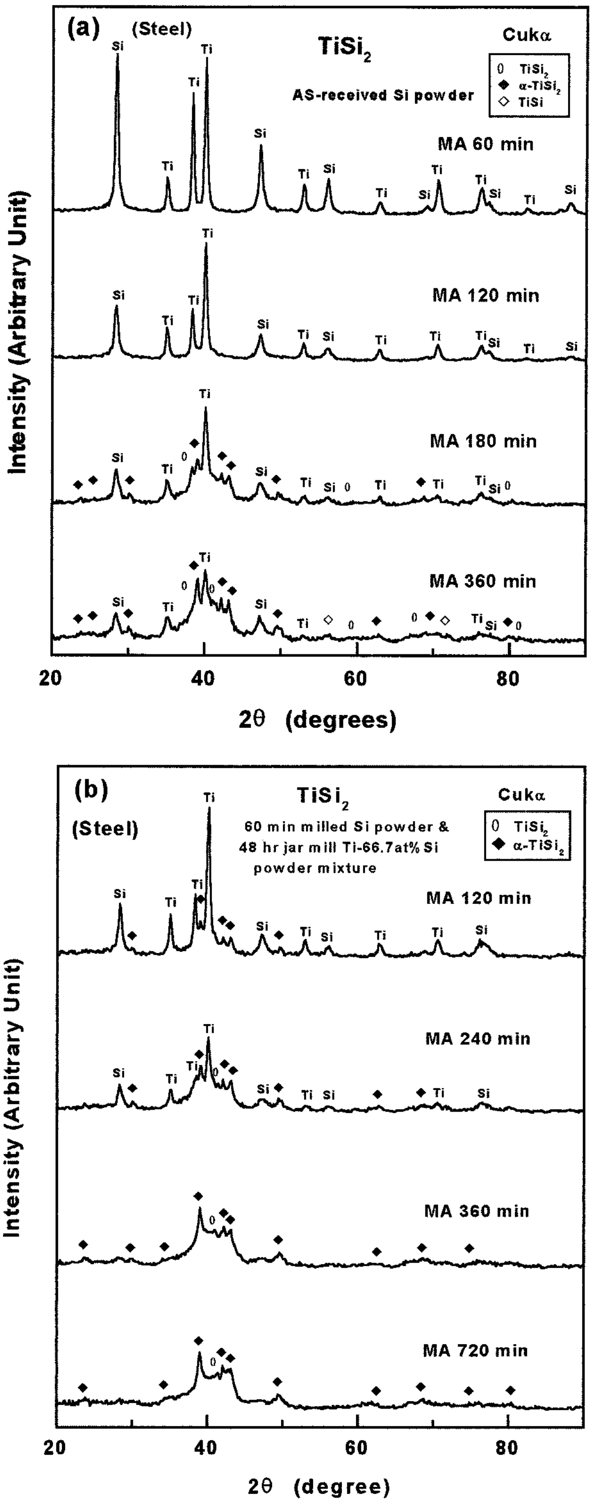

Figure 7 XRD patterns of the PSZ ball-milled Ti-66.7 at. % Si powder mixture in a steel vial at various MA times (a) as-received Si powder and (b) 60 min premilled Si powder and 48 hr jar-milled powder mixture.

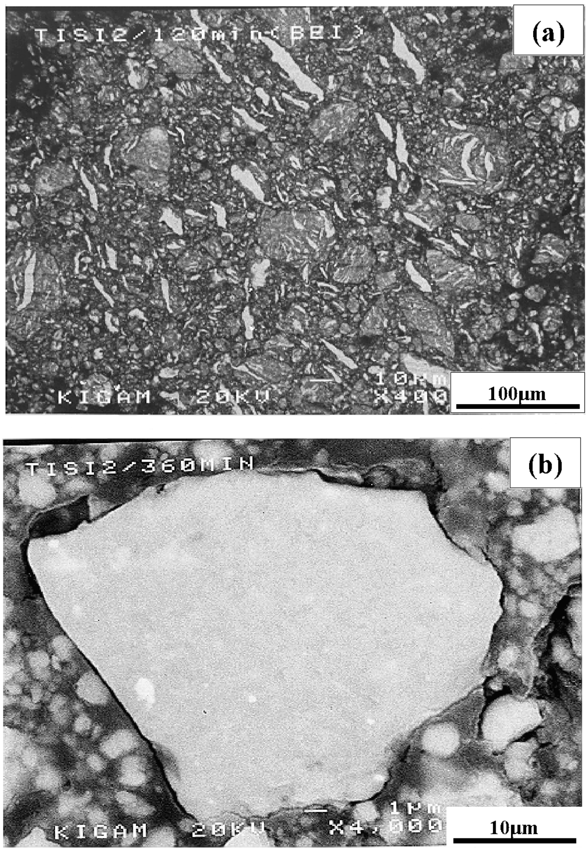

Figure 8 SEM micrographs of cross-sectional Ti-66.7 at. % Si powders mechanically alloyed for 360 min by means of a steel vial and PSZ balls (a) as-received Si powder and (b) 60 min premilled Si powder and 48 hr jar-milled powder mixture.

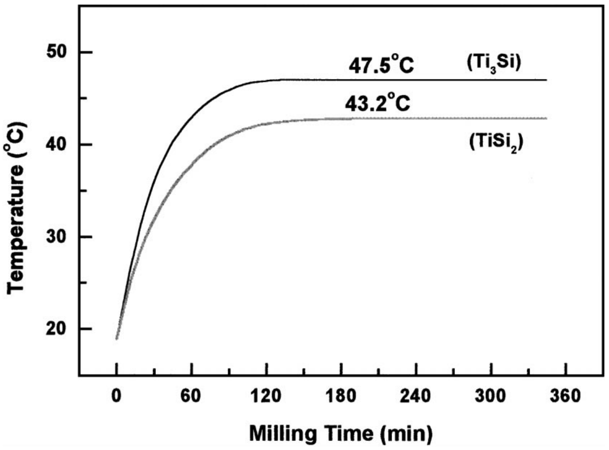

Figure 9 *In-situ* thermal analysis of Ti-25.0 at. % Si and Ti-66.7 at. % Si powders with respect to milling time.

MA time up to 360 minutes, no exothermic reactions have been observed in both cases.

The lack of transformation to Ti_3Si and $TiSi_2$ by ball-milling through an instant exothermic reaction can be ascribed to the following; insufficient critical temperature caused by mechanical impact for the combustion reaction to occur in the powder mixture and insufficient heat transfer between powder particles as well as relatively low negative values of the heat of formation of both Ti_3Si and $TiSi_2$ compared to Ti_5Si_4, Ti_5Si_3, and TiSi (Table I). A larger value of the heat of formation accelerates the transformation to titanium silicide in a shorter ignition time. The formation of Ti_3Si and $TiSi_2$ by mechanical alloying thus occurs through a slow solid state diffusion reaction mechanism induced by mechanical impact between the balls and powders. It was also found that the particle size of Si, degree of powder mixing, and milling medium materials affect the syntheses of Ti_3Si and $TiSi_2$ by mechanical alloying.

In the present study, titanium silicides such as Ti_5Si_4, Ti_5Si_3, and TiSi were obtained by MA through a SHS reaction mechanism. On the other hand, the formation of Ti_3Si and $TiSi_2$ occurs through a slow solid state diffusion reaction mechanism.

4. Summary and Conclusions

Formation mechanisms of titanium silicides by mechanical alloying have been investigated in this work. The critical milling periods for the formation of Ti_5Si_4, Ti_5Si_3, and TiSi were determined to be 22.0, 35.5 and 53.5 min, respectively by *in-situ* thermal analyses. The formation of those products proceeds through a rapid self-propagating high temperature synthesis reaction mechanism.

On the other hand, complete transformation to Ti_3Si and $TiSi_2$ has not been obtained with milling periods up to 360 minutes, due to the lack of homogeneity of the powder mixtures. By introducing finer Si powder and more conductive milling medium materials such as a steel vial instead of a partially stabilized zirconia vial, it was possible to synthesize Ti_3Si and $TiSi_2$. *In-situ* thermal analyses, however, showed that no exothermic reactions occurred during ball-milling. The formation mechanism of Ti_3Si and $TiSi_2$ by mechanical alloying is thus through a slow solid state diffusion reaction.

In conclusion, the formation of titanium silicides by mechanical alloying and the reaction rates depend on several variable parameters such as homogeneity of the powder mixture, milling medium materials, and heat of formation of the product involved.

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